THE PHYSICAL SOCIETY

MEMOIRS

OF THE

COLLEGE OF SCIENCE

KYOTO IMPERIAL UNIVERSITY

VOL. III, No 1.

DECEMBER 1917

KYOTO

On the Beckmann Rearrangement. VIII.

By

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(Received Sept. 18, 1917.)

1. Function of Hydrochloric Acid in the Rearrangement of Acetyloximes.

As a matter of fact it is true that the acyl ester of oxime which contains the acyloxyl radical derived from a strong acid such as benzenesulphonic acid spontaneously suffers the Beckmann rearrangement, while in the case of an ester containing the acyloxyl radical from a weak acid like acetic acid the rearrangement does not take place at all without the aid of hydrochloric acid[1]. Although in the latter case it has been noticed that hydrochloric acid actually takes part of rearrangement[2], how it plays a rôle in reaction has not been fully explained as Stieglitz states[3]: "Beyond suggesting that the hydrochloric acid helps out the weak acetic acid residue in its tendency to exchange positions with the phenyl radical, Kuhara does not explain how the formation of the hydrochloride should facilitate the rearrangement." Recently the authors have, however, been led to declare that the rearrangement which acetyldiphenylketoxime undergoes under the influence of hydrochloric acid must be due practically to the migration of the chlorine radical derived from hydrochloric acid, but not of acetoxyl, as it is highly probable that the chlorine in hydrochloric acid would

1 Kuhara and Kainosho, Mem. Coll. Sci. Eng., Kyoto, **1**, 254 (1903–1908); Kuhara and Todo: Ibid., **2**, 387 (1909–1910); Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, **1**, 105 (1914); Kuhara and Watanabe: Ibid., **1**, 349 (1916); Kuhara and Ishikawa: Ibid., 355 (1910).

2 Kuhara and Kainosho, Mem. Coll. Sci. Eng., Kyoto, **1**, 254 (1903–1908); Henrich and Ruppenthal, Ber. D. chem. Ges., **44**, 1533 (1911).

3 Stieglitz and Stagner, J. Amer. chem. Soc., **38**, 2056 (1916).

replace acetoxyl under the liberation of acetic acid. The scheme of rearrangement may, therefore, be shown as follows:

$$\begin{matrix} C_6H_6.C.C_6H_5 \\ \| \\ HCl,N.OCO.CH_3 \end{matrix} \quad -HOCO.CH_3 \quad \begin{matrix} C_6H_5.C.C_6H_5 \\ \| \\ Cl.N \end{matrix} \quad \rightarrow \quad \begin{matrix} Cl.C.C_6H_5 \\ \| \\ C_6H_5.N \end{matrix}$$

In such a course of reaction it is altogether impossible according to the previous works by one of us and his collaborators as already mentioned[1], to isolate a chlorine compound in the form of chlorimidobenzophenone or phenylbenzimido-chloride, as the reaction progresses to the extreme thus far as to the formation of the final product, i.e, benzanilide, while by treating acetyldiphenylketoxime with benzenesulphonic acid which is nearly as strong as hydrochloric acid, the authors have succeeded to isolate phenylbenzimido-benzenesulphonate which corresponds to phenylbenzimido-chloride in constitution and other respects:

$$\begin{matrix} C_6H_5.C.OSO_2.C_6H_5 \\ \| \\ N.C_6H_5 \end{matrix} \qquad \begin{matrix} C_6H_5.C.Cl \\ \| \\ N.C_6H_5 \end{matrix}$$

Phenylbenzimido-benzenesulphonate — Phenylbenzimido-chloride

In the experiment equivalent quantities of acetyldiphenylketoxime and dehydrated benzenesulphonic acid were heated together to fusion, in which process an explosive violent reaction took place at 95–97° under the evolution of acetic acid, and the whole mass changed to a brownish yellow viscid liquid which was found to change instantly to benzanilide by the addition of water and to possess all other properties of phenylbenzimido-benzenesulphonate[2] obtained by the rearrangement of benzenesulphonyldiphenylketoxime as well as by synthesis. Thus, the reaction may be interpreted as follows:

$$\begin{matrix} C_6H_5.C.C_6H_5 \\ \| \\ C_6H_5.SO_2OH,N.OCO.CH_3 \end{matrix} \quad -HOCO.CH_3 \quad \rightarrow \quad \begin{matrix} C_6H_5.C.C_6H_5 \\ \| \\ N.OSO_2.C_6H_5 \end{matrix}$$

$$\longrightarrow \quad \begin{matrix} C_6H_5.C.OSO_2.C_6H_5 \\ \| \\ N.C_6H_5 \end{matrix}$$

Now it is no doubt that in such a reaction the benzenesulphoxyl group would take possession of the place of the acetoxyl radical, and

[1] Loc. cit.

[2] Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci. Kyoto, I, 105 (1914).

then itself plays a part of rearrangement by its migration on account of its strong negativity; hence the action of hydrochloric acid upon acetylketoxime for effecting its rearrangement may be assumed to be analogous to that of benzenesulphonic acid.

Further, the assumption that the movement of chlorine derived from hydrochloric acid would be a cause of rearrangement may also be supported by the rearrangement of the hydrochloride of oxime through dehydration. Kötz and Wunsdorf[1] mention that the hydrochlorides of acetoxime and acetophenoxime suffer the Beckmann rearrangement under the influence of heat, but no details are given in their article. Thus, the authors have conducted an analogous experiment by using the hydrochloride of diphenylketoxime[2] and have noticed that it changes instantly to benzanilide by heating at 128°, and also by passing dry hydrochloric acid gas through the fused diphenylketoxime at 125°. So, the formation of benzanilide in such experiments may be ascribed to the rearrangement of the chlorine compound formed by the dehydration of the hydrochloride of oxime, the reaction being highly probable to be analogous to that which would occur between acetyloxime and hydrochloric acid or benzenesulphonic acid, as will be seen in the following scheme:

$$\begin{array}{c} R.C.R \\ \| \\ HCl,N.OH \end{array} \xrightarrow{-H_2O} \begin{array}{c} R.C.R \\ \| \\ N.Cl \end{array} \rightarrow \begin{array}{c} R.C.Cl \\ \| \\ N.R \end{array} \rightarrow \begin{array}{c} R.CO \\ \| \\ NHR \end{array}$$

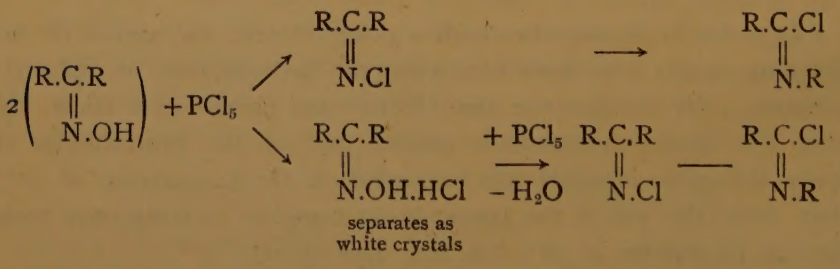
In order to inquire after such a point of view, the action of dehydrating agents have heen tried upon the hydrochloride of diphenylketoxime. For this purpose zinc chloride and chloral were taken; by using the former substance a greater part of the hydrochloride of diphenylketoxime changed into benzanilide at the temperature of 90°, while with the aid of the latter almost complete rearrangement took place in 10 minutes at 90°, but in 2 days at 25°.

Furthermore, the hydrochloride of diphenylketoxime methyl ether, $(C_6H_5)_2C{:}N.OCH_3.HCl$[3], has been observed by the authors to decompose into diphenylketoxime and methyl chloride by heating above its melting point 45°, without undergoing even a trace of rearrangement. Since in this case the methoxy group can not split up as alcohol by

1 Kötz and Wunsdorf, J. prac. Chem., 88, 519 (1913).
2 Spiegler, Ber. D. chem. Ges., 17, 812 1884).
3 Ibid.

the action of hydrochloric acid but as methyl chloride, as is generally known, the formation of the chlorimido group $>NCl$ which is assumed as a necessary factor of rearrangement would be impossible. Such a fact may, therefore, give a support indirectly in the favour of the view that the hydrochloride of diphenylketoxime would form chlorimidodiphenylketone as an intermediate product by dehydration.

According to Henrich and Ruppenthal[1] it is almost clear that hydrochloric acid actually enters into reaction in the Beckmann rearrangement of oxime by phosphorus pentachloride, its hydrochloride being formed as an intermediate product. Thus, gradually adding phosphorus pentachloride, as they state, to a solution of diphenylketoxime in absolute ether, the former at first disappears and then the hydrochloride of oxime separates out as white crystals. After the whole of a definite quantity (equivalent) of phosphorus pentachloride has been added there deposits a yellow chlorine compound which yields benzanilide by the action of water. The authors now interpret such a process of rearrangement as originating partly from the movement of the chlorine radical derived from phosphorus pentachloride by the substitution of the hydroxyl group in oxime and partly from that of the chlorine derived from the hydrochloride through dehydration by phosphorus pentachloride, that is, the rearrangement as being due to that of the chlorine compound containing the chlorimido group $>NCl$ after all, thus the scheme of interpretation being represented as follows:



2. Rearrangement of Chlorimidodiphenylketone containing so called Hypochlorous Chlorine.

Peterson has obtained chlorimidodiphenylketone (chlorimidobenzophenone), $(C_6H_5)_2C{:}N.Cl$, by the action of hypochlorous acid upon imidodiphenylketone hydrochloride, $(C_6H_5)_2C{:}NH.HCl$, and also the

[1] Henrich and Ruppenthal: Ibid., 44, 1533 (1911).

stereoisomeric chlorimides[1]. Stieglitz mentions[2] that "Kuhara's view that the weak negative character of the acetic acid residue is responsible for the rearrangement of acetylbenzophenonoxime without the aid of hydrochloric acid seems to be contradicted by the peculiar fact that all attempts to rearrange chlorimidobenzophenone, $(C_6H_5)_2C{:}NCl$, have failed to indicate the least trace of rearrangement." and also repeated in the following words[3]: "Chlorimidobenzophenone, $(C_6H_6)_2C{:}N.Cl$ has resisted every effort to effect its rearrangement and the same is true of the stereoisomeric chlorimides, $(C_6H_5)(XC_6H_4)C{:}N.Cl$. If the theory of direct exchange were correct, these substances, above all others, should show a spontaneous exchange of the aryl and halogen radicals. It is true, however, that it is still possible that the favorable medium has not yet been discovered for effecting the rearrangement of these compounds,"

According to the authors' recent investigation, however, chlorimidobenzophenone prepared by the method suggested by Peterson[4] seems in fact to suffer rearrangement through the action of alkali. Thus, by subjecting the mixture of chlorimidobenzophenone and caustic potash to fusion an explosive violent reaction took place, yielding a dark brown mass with the decomposition of a great part of the substance and at the same time evolving the dense fume of diphenylketone. The fused mass thus produced was then subjected to the steam distillation, and the distillate tested with a solution of bleaching powder which was observed to give distinctly the characteristic colour reaction of aniline although in a feeble state. Also the same product mixed with some alcohol and a few drops of chloroform was found to evolve the characteristic smell of isonitrile in a remarkable degree by heating[5]. Trying the similar experiments, however, with diphenylketoxime and imidodiphenylketone (hydrochloride) which do not contain the chlorimido group, : NCl, there was no indication of their rearrangement at all, as even a trace of aniline has not been detected. Now it is in-

1 Peterson, Amer. chem. J., 46, 325 (1911).

2 Stieglitz and Stagner, J. Amer. Chem. Soc., 38, 2056 (1916). It is also stated by them that heat, bases, chlorine, phosphorus pentachloride have been tried (ibid., foot note), and again by Vosburgh that five attempts were made to rearrange benzophenonechlorimide but all were unsuccessful (ibid., 2094).

3 Stieglitz and Stagner, J. Amer. Chem. Soc., 58, 2059 (1916)

4 Loc. cit.

5 The authors have repeated Vosburgh's soda lime experiment (loc. cit.), but isonitrile has not been detected, while observed in the potash fusion.

conceivable that aniline could newly be built up from the products of decomposition, so it should be considered as being formed as the result of rearrangement; therefore, it may be concluded that chlorimidodiphenylketone would suffer rearrangement in which the presence of the chlorine linked to the nitrogen atom must be a necessary factor.

Such an unreadiness of the rearrangement of chlorimidodiphenylketone containing the hypochlorous chlorine may be explained by the assumption that its tendency to dissociate from the nitrogen atom would be too feeble, for its specific character is positive, while the chlorimidodiphenylketone supposed to contain the negative chlorine derived from phosphorus pentachloride or hydrochloride acid would suffer rearrangement with excessive readiness, so that it can not be isolated as an intermediate product[1]. The arrangement, therefore, which the chlorimidodiphenylketone containing the hypochlorous chlorine suffers by the alkali fusion must be ascribed to the change of the positive character of its chlorine to the negative under the influence of alkali. As soon as the chlorine radical gets the negative character, naturally its migration should instantly occur like the negative chlorine radical from other sources as well as the negative benzenesulphoxyl radical[2] with the simultaneous shifting of the phenyl group. So, it may be said that Kuhara's assumption respecting the movement of the negative radical would not be inconsistent with Stieglitz's electronic interpretation; now the authors have to represent the plan of rearrangement for the present as follows:

$$\mathrm{R.C.R} \;\underset{\mathrm{N.Cl}}{\overset{+}{\|}} \xrightarrow{\mathrm{KOH}} \mathrm{R.C.R} \;\underset{\mathrm{N.Cl}}{\overset{-}{\|}} \longrightarrow \mathrm{R.C.\bar{Cl}} \;\underset{\mathrm{N.R}}{\|}$$

With regard to the rearrangement of the halogen imido esters (containing the hypochlorous chlorine) by alkali, one of us and Matsui[3]

[1] Beckmann. Ber. D. chem. Ges., 19, 988 (1886); 27, 300 (1894).

[2] Stieglitz states in his electronic interpretation that the acyloxyl radicals in the oxime esters such as $(C_6H_5)_2C{:}N.OCO.CH_3$ and $(C_6H_5)_2C{:}N.OSO_2.C_6H_5$, take the positive charges like $CH_3.CO-O+$ and $C_6H_5.SO_2-O+$, and the rearrangements are assumed to "originate from the tendency of unstable positive atoms Cl+, −O+, −N+ to go over into their stable negative forms Cl−, −O−, N− by capture of electron from other atoms in the same molecule a change which is effected in the rearrangement in question." Thus, if the change of the sign of the positive chlorine or acyloxyl radical were admitted to take place before or simultaneously with the cxchange of radicals, the chlorine or acyloxyl radical which actually migrates should be considered to be practically negative as the authors assume.

[3] Kuhara and Matsui, Mem. Coll. Sci. Eng., Kyoto, 1, 187 (1902–1908).

have put forward an explanation based upon the assumption of Hoogewerff and van Dorp[1], and Jones[2] has also explained the rearrangement of the halogen amides in the presence of alkali "in terms of copascular atomic hypothesis." But the authors' present case of the rearragnement of chlorimidobenzophenone by alkali does not stand in harmony with either of those explanations, so it seems to require an interpretation of some other type.

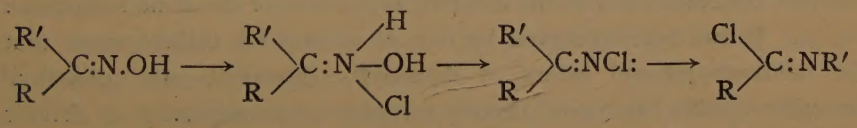
Furthermore, the authors have tried the alkali fusion of acetyldiphenylketoxime, but not a trace of aniline has been detected by the colour reaction; this shows that the acetoxyl radical being of the negative nature, may not change its sign by alkali, so the rearrangement would not take place on account of its weak negativity.

3. Relation of the Stereoisomerism of Oximes to their Products of Rearrangement.

It has been shown by Montagne[3] and also by Jones[4] that the theory of the monovalent nitrogen proposed by Stieglitz meets difficulties in explaining the differences observed in the migration of the hydrocarbon radicals, *R* and *R'*, of stereoisomeric oximes,

$$\begin{array}{c} R.C.R' \\ \| \\ N.OH \end{array} \quad \text{and} \quad \begin{array}{c} R.C.R' \\ \| \\ HO.N \end{array}$$

Thus, Stieglitz[5] has recently brought forward a new interpretion for the rearrangement of oxime which is said by him to be the extension of the original theory, taking analogy with the rearrangement of triphenylmethylhydroxylamine by phosphorus pentachloride as will be seen in the following scheme:



But we may regard such an interpretation to be a modified form of the direct exchange theory, so both may be practically identical.

1 Hoogewerff and van Dorp, Rec. trav. chim., **6**, 375 (1887); **8**, 173 (1889).
2 Jones, Amer. chem. J. **48**, 25–26 (1912).
3 Montagne, Ber. D. chem. Ges., **43**, 2014 (1910).
4 Jones, Amer. Chem. J., **48**, 28 (1912).
5 Stieglitz: Ibid., **18**, 751 (1896).
6 Stieglitz and Leach, J. Amer. Chem. Soc., **36**, 272 (1914).

Now if it is assumed in our direct exchange theory that the dissociation of acid residue in oxime ester which is regarded as a prime factor of rearrangement[1] as we assume, would occur before the migration of the hydrocarbon radical, R or R', there should be no difference in the products of rearrangement as in the case of the movalent nitrogen theory:

$$\begin{array}{ccccc} R.C.R' & & R.C.R' & & R.C.R' \\ \| & \longrightarrow & \| & \longrightarrow & \| \\ N.OH & & N.X & & N|X \end{array}$$

$$\begin{array}{ccccc} R.C.R' & & R.C.R' & & R.C.R' \\ \| & \longrightarrow & \| & \longrightarrow & \| \\ HO.N & & X.N & & X|N \end{array}$$

We have, however, a reason for believing that the exchange of the positions of the acid residue and hydrocarbon radical, R or R', immediately opposite to the acid residue would take place *simultaneously*. Hence, if we admit such a view as correct the possibility of the different products of rearrangement could readily be explained:

$$\begin{array}{ccccc} R.C.R' & & R.C.R' & & R.G \,|\, R' \\ \| & \longrightarrow & \| & \longrightarrow & \| \;\; \uparrow\downarrow \\ N.OH & & N.X & & N \,|\, X \end{array}$$

$$\begin{array}{ccccc} R.C.R' & & R.C.R' & & R \,|\, C.R' \\ \| & \longrightarrow & \| & \longrightarrow & \uparrow\downarrow \;\; \| \\ HO.N & & X.N & & X \,|\, N \end{array}$$

Such a conception respecting the simultaneous occurrence of the mutual exchange of radicals originates, as will be seen, from the results of investigation on the rearrangement of the same acyl esters of the different ketoximes and of the different acyl esters of the same ketoxime:

1. It has been observed by one of us and his collaborators that the benzenesulphonyl esters of diphenyl[2], dibenzyl[3] and dimethyl[4] ketoximes suffer at once almost complete reareangement at definite temperatures respectively, that is to say, conduct the exchange of radicals more or less readily according to the nature of the hydrocarbon radicals linked to the carbon atom of the diaryl or dialkyl methane

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1 Loc. cit.

2 Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, **1**, 105 (1914).

3 See the experimental part.

4 Ibid.

nucleus, judging from the structural point of view, namely in the order of phenyl, benzyl and methyl as will be seen:

(1)	(2)	(3)
$C_6H_5.C.C_6H_5$ $\|\|$ $N.OSO_2.C_6H_5$	$C_6H_5.CH_2.C.CH_2.C_6H_5$ $\|\|$ $N.OSO_2.C_6H_5$	$CH_3.C.CH_3$ $\|\|$ $N.OSO_2.C_6H_5$
Rearranges at 62° (M. p. 62°)	Rearranges at 74° (M. p. 64°)	Rearranges at 130° (M. p. 52–53°)

Hence it is evident that the hydrocarbon radicals would exert some influence upon the migration of the benzenesulphoxyl group, since the latter moves more or less readily in the benzenesulphonyl esters of the different ketoximes, while the group, $>C{:}N.OSO_2C_6H_5$, is common to those oxime esters.

2. Comparing the rates of rearrangement of benzenesulphonyl esters of diphenylketoxime, phenylmethylketoxime and ethylsynbenzhydroximic acid in which the phenyl and benzenesulphoxyl groups equally occupy the positions directly opposite to each other:

(1)	(2)	(3)
$C_6H_5.C.C_6H_5$ $\|\|$ $N.OSO_2.C_6H_5$	$CH_3.C.C_6H_5$ $\|\|$ $N.OSO_2.C_6H_5$	$C_2H_5O.C.C_6H_5$ $\|\|$ $N.OSO_2.C_6H_5$
Rearranges at 62° (M. p. 62°)	Rearranges at 81–82° (M. p. 60–61°)	Rearranges at 95–96° (M. p. 54–55°)

it may be admitted as true that the rearrangement would occur more or less readily according to the nature of the hydrocarbon and alkoxyl radicals, that is, in the order of phenyl, methyl and ethoxyl linked to the same carbon atom with which the phenyl group directly opposite to the benzenesulphoxyl combines.

It may, therefore, be concluded that the phenyl, methyl and ethoxyl groups would exert an influence differently upon the movement of benzenesulphoxyl and phenyl immediately opposite to it, as the molecular structures of 3 esters are identical excepting 3 respective radicals, i.e, C_6H_5, CH_3 and C_2H_5O.

3. Looking upon the rearrangement of several different acyl esters of diphenylketoxime whose acyloxyl groups have been derived from the acids of different strengths, such as *m*-nitrobenzenesulphonic, ben-

zenesulphonic, monochloracetic and acetic acids[1], it has also been noticed by one of us and his collaborators that they suffer rearrangement more or less readily according to the strength of the negative character of acyloxyl as will be shown in the following table :

(1)	(2)
$C_6H_5.C.C_6H_5$ $\|\|$ $N.OSO_2.C_6H_4.NO_2(m)$	$C_6H_5.C.C_6H_5$ $\|\|$ $N.OSO_2.C_6H_5$
Rearranges at 24° (M. p. 24°)	Rearranges at 62° (M. p. 62°)
(3)	**(4)**
$C_6H_5.C.C_6H_5$ $\|\|$ $N.OCO.CH_2Cl$	$C_6H_5.C.C_6H_5$ $\|\|$ $N.OCO.CH_3$
Rearranges above 195° (M. p. 140°)	Not rearranges (M. p. 71°)[2]

So, the readiness and difficulty of exchange of radicals in the different acyl esters of diphenylketoxime are evidently dependent upon the strength of the negative character of the acyloxyl radical attached to the nitrogen atom, as the group $(C_6H_5)C{:}N.$ is common to all of those acyl esters.

Now a conclusion may be drawn as follows :

Since the acyloxyl and hydrocarbon radicals in the acyl esters of ketoximes are not independent from each other in partaking of rearrangement, but seem to exert mutually their influences for the exchnge of their positions, the most conceivable assumption to be put forward is that *the exchange of radicals would be simultaneous.*

EXPERIMENTAL PART.

1. Action of Benzenesulphonic Acid upon Acetyldiphenylketoxime

A mixture of equivalent quantities of acetyldiphenylketoxime and dehydrated benzenesulphonic acid was heated to fusion. Continuing

[1] Kuhara and Todo, Mem. Coll. Sci. Eng., Kyoto, **2**, 388 (1909–1910). *m*-Nitrobenzenesulphonic acid must be much stronger than benzenesulphonic acid, judging from its constitutional point of view.

[2] Kuhara and Kainosho have found the melting point to be 71°, while Spiegler mentions as 55°. Mem. Coll. Sci. Eng., Kyoto, **1**, 261 (1903–1908); Monatsh. Chem., **5**, 205.

the heating the mixture suddenly changed into a dark yellow viscid mass at 95–97° with explosive violence under evolution of acetic acid. The product of reaction or viscid substance was treated with chloroform, by which process there was left some insoluble matter, giving a brownish yellow solution. The solution by evaporation gave a brownish yellow viscid liquid as a residue. The latter was observed to change at once into benzanilide by the action of water, and also showed the identity in other properties with phenylbenzimido-benzenesulphonate[1], $C_6H_5.C(OSO_2.C_6H_5):N.C_6H_5$, obtained synthetically by the action of silver benzenesulphonate upon phenylbenzimido-chloride as well as by the rearrangement of diphenylketoxime benzenesulphonyl ester. Further, it was noticed that diphenylketoxime itself suffers the similar change under the similar treatment with benzenesulphonic acid.

2. *Action of Heat and of Dehydrating Agents upon Diphenylketoxime Hydrochloride.*

Diphenylketoxime hydrochloride[1] was prepared by passing a slow current of hydrochloric acid gas through an etherial solution of diphenylketoxime at 0°, separating out as white crystalline precipitate. The identification of the substance was made by its decomposition into components by the action of water, alkali or alkaline carbonate, and by its analysis.

0.289 grm. of the hydrochloride gave 0.172 grm. AgCl.

	Calc. as $(C_6H_5)_2C:N.OH.HCl$	Found
Chlorine	15.18	14.81

The hydrochloride fused at 128°, producing a colourless watery liquid, which on continuing the heating at the same temperature at first coloured slightly yellow evolving hydrochloric acid gas, and then changed at once into almost colourless crystalline mass under violent reaction. By repeating the recrystallization of the latter from aqueous alcohol we got the scaly crystals of pearly luster, which were confirmed to be benzanilide by its melting point and other properties. The same reaction was observed to take place at 125° by passing a current of hydrochloric acid into the heated oxime, producing 95% of the theoretical yield of benzanilide.

[1] Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, I, 105 (1914).

[2] Loc. cit.

With regard to the use of dehydrating agents the following experiments were carried out:

By heating a mixture of diphenylketoxime hydrochloride and finely powdered zinc chloride in a small flask immersed in a glycerine bath, it softened at about 60°. Now a part of contents of the flask was taken out and examined for benzanilide, but we could not recognize its production at all. Elevating the temperature, however, its production was observed with a gradual increase. Thus at 70° some was observed to have been produced, while at 90° almost whole of the hydrochloride to have suffered rearrangement.

By using chloral as a dehydrating agent, rearrangement was found to take plece much more readily. In such a case diphenylketoxime hydrochloride was dissolved in a small quantity of chloral and the solution heated at 90° for 10 minutes, by which the colourless solution changed slightly yellow. Now after cooled, a solution of caustic soda was added in order to effect the decomposition of chloral. By warming the mixture chloroform produced was expelled, and the oxime escaped from reaction and sodium formate formed passed into solution, and benzanilide remained as precipitate which was separated by filtration, washed and recrystallized from aqueous alcohol. 0.378 grm. of the hydrochloride gave 0.287 grm. benzanilide, hence its yield was found to be 91% of the theoretical. It was also noticed that almost complete rearrangement took place when the mixture of the hydrochloride and chloral was kept at 25° in a thermostatt for two days and at a lower temperature for a week.

3. *Decomposition of the Hydrochloride of Diphenylketoxime Methyl Ether by Heat.*

Diphenylketoxime methyl ether, $(C_6H_5)_2C{:}N.OCH_3$, was prepared according to the method by Spiegler[1]. It was changed to its hydrochloride by passing a current of hydrochloric acid gas through its etherial solution with a special precaution, as the hydrochloride is soluble in ether in presence of the excess of the acid.

By heating the hydrochloride above its melting point, it was noticed to decompose into diphenylketoxime and methyl chloride as is usually concerned of the compounds containing the methoxyl group, and to show not a trace of the indication of rearrangement.

1 Loc. cit.

4. Rearrangement of Chlorimidodiphenylketone.

Chlorimidodiphenylketone (Chlorimidobenzophenone)[1], $(C_6H_5)_2C{:}NCl$, has been prepared according to Peterson's statement. By fusing an intimate mixture of chlorimidodiphenylketone and caustic potash each in finely powdered state, an explosive violent reaction took place yielding a dark brown mass under the decomposition of the greater part of the substance, and at the same time evolving a dense fume of benzophenone in a considerable quautity. A part of the reaction product was mixed with some alcohol and a few drops of chloroform, and then heating the mixture the characteristic smell of isonitrile was noticed in a remarkable degree. Now subjecting the same product to the steam distillation the aqueous distillate was observed to contain a small quantity of aniline, giving the characteristic violet colouration by the solution of bleaching powder although in a feeble state. The fume of benzophenone evolved in the reaction as above stated, when passed into water and tested with the bleaching powder solution, was also found to give the colour reaction of aniline.

Imidodiphenylketone hydrochloride, $(C_6H_5)_2C{:}NH.HCl$, diphenylketoxime, $(C_6H_5)_2C{:}NOH$ and acetyldiphenylketoxime, $(C_6H_5)_2C{:}N.OCO.CH_3$, however, under the similar treatment with caustic potash gave no reaction of aniline and isonitrile.

5. Rearrangement of Dibenzylketoxime Benzenesulphonyl Ester.

Dibenzylketoxime, $(C_6H_5CH_2)_2C{:}N.OH$, prepared from dibenzylketone[2], following the method of preparation of diphenylketoxime[3], was converted into its sodium salt by means of metallic sodium, and the salt thus obtained into benzenesulphonyl ester, $(C_6H_5CH_2)_2C{:}N.OSO_2.C_6H_5$ by the usual method as often described. The ester consists of colourless crystals and has been found to melt at 64°, being soluble in alcohol, benzene and chloroform. It was analysed and gave the following value for sulphur.

0.135 grm. substance gave 0.0864 grm. $BaSO_4$

	Calc. for $(C_6H_5CH_2)_2C{:}N.OSO_2.C_6H_5$	Found
Sulphur	8.78	8.79

1 Loc. cit.
2 Apitzsch, Ber. D. chem. Ges., **37**, 1429 (1904).
3 Loc. cit.

The ester changed into a yellow viscid liquid by gradual heating, while an explosive violent reaction spontaneously occured at 74° under decomposition. The yellow viscid substance which consists mainly of the rearrangement product or benzylphenylacetimido-benzenesulphonate, $C_6H_5.CH_2.C(OSO_2.C_6H_5):N.CH_2.C_6H_5$, readily changed into benzylphenylacetamide, $C_6H_5.CH_2.CONH.CH_2.C_6H_5$, and benzenesulphonic acid by treating with water. Benzylphenylacetamide was confirmed by comparison with the melting point and other properties of the same substance especially prepared by the authors by synthesis, and benzenesulphonic acid by analysis of its barium salt.

0.268 grm. unhydrous barium salt gave 0.138 grm. $BaSO_4$.

	Calc. for $(C_6H_5.SO_2O)_2Ba$	Found
Barium	30.42	30.30

Now the course of reaction would no doubt follow our rule as will be seen:

$$C_6H_5CH_2.C(N.OSO_2.C_6H_5).CH_2.C_6H_5 \xrightarrow{74^\circ} C_6H_5.CH_2.C(N.CH_2.C_6H_5).OSO_2.C_6H_5$$

$$\xrightarrow{H_2O} C_6H_5.CH_2.CO.NH.CH_2.C_6H_5 + C_6H_5.SO_2OH$$

Benzylphenylacetamide has been synthetically prepared by the action of phenylacetyl chloride upon an etherial solution of benzylamine. It crystallizes from alcohol in colourless scales and melts at 118–119°, and readily soluble in alcohol, slightly in ether and not in water. By heating with concentrated hydrochloric acid for a few hours in a sealed tube at 150–160° it spilits up into its components, i.e., phenylacetic acid and benzylamine. The substance gave the following value for nitrogen by analysis,

0.193 grm. substance gave 10.2 c.c. nitrogen at 15° and 765 mm.

	Calc. for $C_6H_5CH_2.CONH.CH_2C_6H_5$	Found
Nitrogen	6.22	6.27

The authors have also prepared acetyl and benzoyl esters of dibenzylketoxime, i.e., $(C_6H_5.CH_2)_2C:N.OCO.CH_3$ and $(C_6H_5CH_2)_2C:N.OCO.C_6H_5$, by the similar method and studied their behaviours, Both are colourless crystalline substances, and soluble in alcohol, ether and chloroform. The acetyl ester melts at 33–34° and the benzoyl at 60.5°. By heating they do not show an indication of rearrangement.

6. *Rearrangement of Diphenylketoxime m-Nitrobenzenesulphonyl Ester.*[1]

Diphenylketoxime *m*-nitrobenzenesulphonyl ester, $(C_6H_5)_2C{:}N.OSO_2.C_6H_4.NO_2$, has been prepared from the sodium salt of diphenylketoxime by the action of *m*-nitrobenzenesulphonyl chloride[2] according to our method of preparation of the oxime esters[3]. The substance crystallizes out when an etherial solution of the reaction product has been evaporated by passing a current of dry air through it keeping the temtemperature below 24°. The substance was analysed and gave the following value for sulphur.

0.1354 grm. substance gave 0.0792 grm. $BaSO_4$

	Calc. for $(C_6H_5)_2C{:}N.OSO_2.C_6H_4.NO_2$	Found
Sulphur	8.39	8.03

The substance, melting at 24°, suffered the spontaneous rearrangement instantaneously with a hissing noise yielding a yellow viscid liquid like other oxime esters. The product of rearrangement or viscid substance, $C_6H_5.C(OSO_2.C_6H_4.NO_2){:}N.C_6H_5$, decomposed into benzanilide and *m*-nitrobenzenesulphonic acid quickly by treating with water, while slowly on allowing it to stand itself in open air. Of two products of decomposition, benzanilide has been identified by its properties, and *m*-nitrobenzenesulphonic acid[4] by the analysis of its barium salt.

0.1844 grm. substance gave 0.077 grm. $BaSO_4$.

	Calc. for $(C_6H_4.NO_2.SO_2.O)_2Ba$	Found
Barium	24.54	24.57

Thus, the course of rearrangement would be:

$$C_6H_5.C(N.OSO_2.C_6H_4.NO_2).C_6H_5 \xrightarrow{24^\circ} C_6H_5.C(N.C_6H_5).OSO_2.C_6H_4.NO_2$$

$$\xrightarrow{H_2O} C_6H_5.CO.NH.C_6H_5 + NO_2C_6H_4.SO_2OH$$

1 Unpublished work with Matsunami.
2 Limpricht, Lieb. Ann.. 177, 65 (1875).
3 Loc. cit.
4 Limpricht, Lieb. Ann., 177, 60 (1872).

7. Rearrangement of Dimethylketoxime Benzenesulphonyl Ester.[1]

Dimethylketoxime benzenesulphonyl ester, $(CH_3)_2C{:}N.OSO_2.C_6H_5$, has been prepared by Wege[2] by the action of benzenesulphonyl chloride upon dimethylketoxime in presence of aqueous alkali. The ester forms large colourless crystals and melts at 52–53°. By heating to 130° the reaction occurred with explosive violence under decomposition, and the product by treating with alkali liberated methylamine which was received in hydrochloric acid. The hydrochloride of methylamine was converted into platinum double salt, and analysed.

I. 0.092 grm. double salt gave 0.038 grm. platinum.
II. 0.068 „ „ „ „ 0.028 „ „

	Calc. for $(CH_3.NH_2.HCl)_2PtCl_4$	Found I	Found II
Platinum	41.34	41.30	41.17

Now it is evident that the ester has suffered rearrangement; but all the efforts to isolate methylacetamide which must be the product of rearrangement were unsuccessful.

8. Rearrangement of Diphenylketoxime Chloracetyl Ester.

Diphenylketoxime chloracetyl ester $(CH_3)_2C{:}N.OCO.CH_2Cl$, has been prepared by our method from the sodium salt of diphenylketoxime by the action of chloracetyl chloride. The ester forms colourless crystals and melts at 24°. It suffered rearrangement under decomposition by heating above 195°, and from the product of reaction benzamilide has been isolated.

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[1] Unpublished work with Yura.

[2] Wege, Ber. D. chem. Ges., **24**, 3537 (1871).

Vol. III., No. 1, Published December 18th, 1917.

Price - - - Yen 0.15

These Memoirs are on sale at

MARUZEN COMPANY, LTD.

TOKYO, OSAKA, KYOTO, FUKUOKA & SENDAI.

大正六年十二月十五日印刷

大正六年十二月十八日發行

編纂兼發行者　京都帝國大學理科大學

印刷者　野村宗十郎

東京市京橋區築地三丁目十一番地

印刷所　株式會社東京築地活版製造所

東京市京橋區築地二丁目十七番地

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東京、大阪、京都、福岡、仙臺

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